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(21) International Application Number: PCT/US93/03240 (22) International Filing Date: 7 April 1993 (07.04.93) (30) Priority data: 867,836 13 April 1992 (13.04.92) US (71) Applicant: GELTECH, INC. [US/US]; Two Innovation Drive, Alachua, FL 32615 (US). (72) Inventors: NOGUES, Jean-Luc ; 5517 NW 45th Lane, Gainesville, FL 32606 (US). HOWELL, R., Layne ; 5700 NE 83rd Terrace, Gainesville, FL 32606 (US). (74) Agents: FRANK, Steven, J. et al.; Cesari & McKenna, 30 Rowes Wharf, 5th Floor, Boston, MA 02109 (US).		(81) Designated States: CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: GLASS AND CERAMIC COMPONENTS HAVING MICROSCOPIC FEATURES (57) Abstract Monoliths having hyperfine features below 500 microns in at least one dimension are produced using sol-gel processing techniques. The monoliths are molded as lenses, lenslets, lens arrays, gratings, reticles, mold castings, microchannel devices, micromachines, nanomachines and electronic substrates.		

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**GLASS AND CERAMIC COMPONENTS
HAVING MICROSCOPIC FEATURES**

BACKGROUND OF THE INVENTION

A. Field of the Invention

The present invention relates to fine-featured glass articles, and in particular to optical and other monoliths produced using sol-gel technology.

B. Description of the Related Art

Optical and non-optical (e.g., grating, mold and microchannel) components having surface features of dimension 500 microns and below (hereinafter "hyperfine features") can today be fabricated only through the use of expensive processes or from materials that exhibit certain limitations. Because conventional machining techniques for the manufacture of optical components are unsuited to production of very small features, practitioners have turned to photolithography and ion etching to create submillimeter surface features. These processes are not only costly, but can produce only a limited range of feature types. In particular, one cannot etch a smooth concave or convex profile using either of the foregoing techniques, nor can one obtain true prismatic profiles.

It is also possible to obtain submillimeter features by pouring molten material into a suitably featured mold and allowing the material to cool into a solid form. This technique has been used successfully, for example, to produce plastic monoliths. Unfortunately, plastic components suffer from several shortcomings. First, they exhibit large coefficients of thermal expansion and limited mechanical properties, and tend to deteriorate at elevated temperatures. Thus, well before a plastic piece actually melts, its surface

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texture will degrade and its index of refraction may change; either transformation is obviously unacceptable in an optical context, and so plastics cannot operate in hot environments or transmit high-power light (which causes internal heating of the plastic). Plastics also provide a restricted transmission range for optical applications, and their usefulness even within the restricted bandwidth is limited by the tendency to accumulate internal stresses during molding (a condition that results in distortion of transmitted light during use). And finally, many chemical and environmental agents degrade plastics which, as a consequence, are difficult to clean effectively.

We are aware of no attempts to mold hyperfine features into glass. Vitreous material retains significant viscosity at practical working temperatures, which would prevent the molten glass from accurately and reliably conforming to the hyperfine-featured mold. Furthermore, glass undergoes dimensional changes over large temperature variations; accordingly, even if the temperature of the molten glass could be raised to the point of achieving adequate fluidity to permit hyperfine molding, distortions would occur as the glass solidified. In addition, organic and inorganic impurities commonly present in glass can interfere with the molding process as well as degrade the optical purity of the final product.

DESCRIPTION OF THE INVENTION

A. Brief Summary of the Invention

The present invention utilizes sol-gel technology to fabricate monoliths having hyperfine surface features. Ceramic and glass materials have been produced using the sol-gel process for many years. A "sol" is a dispersion of colloidal

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particles in a liquid, and the term "gel" connotes an interconnected, rigid network with pores of submicron dimensions and polymeric chains whose average length is greater than a micron. Basically, the sol-gel process involves hydrolyzing and polycondensing one or more oxide precursors to form a sol comprising a plurality of oxide particles suspended in a liquid; casting the sol into a mold; gelling the mixture, whereby the colloidal oxide particles cross-link together to become a porous three-dimensional network; aging the gel to increase its strength; removing the liquid from the interconnected pore network; and densifying the dry gel (with or without dehydration or chemically stabilization); and densifying the dehydrated precursor, to produce structures with ranges of physical properties. See, e.g., Hench & West, The Sol-Gel Process, 90 Chem. Rev. 33 (1990); and U.S. Patent No. 5,076,980, which is hereby incorporated by reference.

We have found, quite surprisingly, that the sol-gel process can be used to produce monoliths having hyperfine surface features. Despite its utility and convenience, the sol-gel process is known to have certain limitations. Sol-gel monoliths tend to undergo linear shrinkage of 40-75% during processing, due primarily to the syneresis that occurs during drying. Although one can control for such shrinkage in a gross sense by oversizing the mold, some physical distortion has been assumed to be inevitable. In particular, while we are aware of attempts to use the sol-gel process to produce fresnel lenses having features on the order of 0.5mm, we are not aware of any uses of the sol-gel process to obtain finer features.

Using the sol-gel process as described in the '980 patent mentioned above, we have discovered that sol-gel shrinkage is almost entirely isotropic, predictable and reproducible, so that fine features persist with excellent fidelity to the original mold; accordingly, because shrinkage occurs equally in

all directions, it is possible to obtain a monolith with features having a desired size merely by determining the amount of shrinkage produced by a given set of process parameters, and then designing a mold oversized by just this amount. Indeed, such shrinkage is highly advantageous, since the molds need not contain features as fine as those of the final product.

B. Brief Description of the Drawings

The foregoing discussion will be understood more readily from the following detailed description of the invention, when taken in conjunction with the accompanying drawings, in which:

FIG. 1 is an isometric view of a cylindrical lens array;

FIG. 2 is an isometric view of a prismatic lens array;

FIG. 3 is an isometric view of an array of hyperfine lenses having a high fill factor;

FIG. 4 is an isometric view of an array of hyperfine lenses having a low fill factor;

FIG. 5 is an isometric view of a blazed-type hyperfine grating;

FIG. 6 is an isometric view of a sinusoidal-profile hyperfine grating; and

FIG. 7 is an exploded view of a mold assembly suitable for use in conjunction with the present invention.

C. Detailed Description of the Preferred Embodiments

As used herein, the term "hyperfine lens" shall connote a single lens, a lenslet or an array of lenses having smooth,

curved features equal to or less than 500 microns along at least one dimension. The individual lens elements may be concave or convex; spherical, aspherical or fresnel; cylindrical (as shown in FIG. 1) or prismatic (as shown in FIG. 2); and disposed on a planar substrate or on a curved substrate. Arrayed lenses may be produced in various densities. In a "high-fill-factor" array, illustrated in FIG. 3, the lens elements abut or lie close to one another; in a "low-fill-factor" array, illustrated in FIG. 4, the lens elements are spaced apart. In all four figures, the dimension a is equal to or less than 500 microns.

As used herein, the term "hyperfine grating" shall connote a blazed-type grating, as illustrated in FIG. 5, with groove spacing a equal to or less than 500 microns; or a curve-profile grating, as illustrated in FIG. 6, with groove spacing a equal to or less than 500 microns. The groove spacing may be fixed or variable, and the grooves themselves may be disposed on a planar or curved substrate.

Depending on the material chosen, hyperfine gratings may reflect or transmit radiation. The sol-gel process can be used to produce highly transparent glass or relatively opaque ceramics, as described in the '980 patent and as known generally in the art. For example, sol-gel glass can be produced from silicate compositions (including pure silica), while alumina-based compositions can be sintered into ceramics. Furthermore, the amorphous structure of a silicate glass can be converted into a glass-ceramic object (in which small crystalline domains are introduced into the glass matrix) by conventional heat treatments well-characterized in the art. The reflectivity of a monolith can be increased, for example, by metallizing it with several hundred angstroms or less of a reflective metal (e.g., gold or aluminum); the resulting reflective coating does not interfere with the hyperfine

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structure. It can be similarly decreased using less reflective materials.

Using the techniques outlined in the '980 patent, we have produced hyperfine lenses and hyperfine gratings having feature sizes of several hundreds of microns, several tens of microns, several microns and dimensions below one micron. However, by using, for example, the resulting monolith as a cast for a mold and successively repeating this molding and mold-casting process, it is possible to utilize the sol-gel shrinkage in a progressive fashion to obtain monoliths with features as small as 10 nm.

As mentioned above, sol-gel monoliths tend to undergo linear shrinkage of 40-75% during processing. It is possible to control the amount of shrinkage by varying the amount of precursor contained in the sol (e.g., in the case of silica casting, by changing the ratio of silica precursor to solvent). This is a straightforward process, and our preferred linear shrinkage range is 50-70%.

D. Examples

In the following examples, we employed the mold illustrated schematically in FIG. 7. The mold comprised an active surface assembly 10, which included an active surface 12 (as described in the specific examples below) and a polystyrene template 14 machined from a polystyrene sheet. A ring plate 16, also machined from a polystyrene sheet, was mounted on active surface assembly 10 so as to surround active surface 12 during processing. After casting of the sol as described below, we sealed the mold by securing a polycarbonate cover plate 20 over ring plate 16 with TEFLON^(R) tape.

EXAMPLE 1

A solution of 0.2 moles (17.8g) of concentrated nitric acid and 70.15 moles (1262.7g) of deionized water was formed. To this solution, 4.4 moles (669.5g) of TMS was added over 3-5 minutes with continuous stirring. The temperature of the solution was then raised to its boiling temperature, and the solution was allowed to boil for 20 minutes. The solution was then cooled to 50° C or below and cast into a mold, where it was maintained at ambient temperature until gelation occurred (approximately 48 hours). The active surface 12 of the mold used in this example contained a negative surface of a cylindrical lens array with a lens width of 375 microns. The gel formed was placed in an oven at 40° C for 12 hours and then heated at a rate of 4° C/hour to 80° C, which temperature was maintained for 24 hours. The heated gel was cooled to 40° C over one hour and then cooled further at ambient temperature for another hour.

The gel was then transferred to an oven in which the temperature and atmosphere were directly controlled by a microprocessor. Initially, the oven was maintained at a temperature of 40° C and a relative humidity of 99.9%. Once the gel was placed in the oven, the temperature was increased to 99° C over four hours while maintaining the 99% relative humidity. The oven was then kept at 99° C and 99.9% humidity for 2 hours, at which time the temperature was increased to 102° C over 0.5 hour. The temperature was maintained at 102° C for 7.5 hours, during which time small controlled amounts of water were added to the oven using a wet bulb. After 7.5 hours, the temperature was increased to 120° C over an 8 hour period, followed by an increase to 160° C over 4 hours. During the last temperature increase, the oven was purged with very dry, compressed air. After maintaining the temperature at 160° C for two additional hours, the oven was cooled to 120° C over

a one hour period while still being purged with dry air. Before removing the dried gel, the oven was cooled to 40° C

The dried gel was placed on a quartz diffusion boat with a 1 to 2 mm clearance between it and other gels being simultaneously treated. The diffusion boat was then placed in a furnace maintained at a temperature of 80° C, and the furnace was closed. Dry air was flowed through the furnace at 80 SCFH (standard cubic feet per hour).

The following ramp and constant temperature schedule was followed to partially densify the gel:

- 1) the temperature was increased from 80° to 190° C over 6 hours, followed by maintaining the temperature at 190° C for 1 hour;
- 2) the temperature was then increased to 400° C over 9.5 hours, followed by maintaining a temperature of 400° C for 2 hours; and finally
- 3) the temperature was increased to 626° C over 12.5 hours and then to 820° C over 10 hours, followed by maintaining a temperature of 820° C for 10 hours.

The furnace was then cooled down to 80° C over 14.4 hours. The resulting partially densified gel monolith was crack-free.

After the run was complete, the furnace was opened and the gel was removed. The partially densified gel was placed on a quartz ladder which was then placed directly in the center of a controlled atmosphere furnace. A heat barrier was placed in the front end of the furnace tube, and an end cap was placed on the end. The joints were then sealed with non-stick tape made from a TEFLON^(TM) polymer. The furnace was equipped with a system to avoid retrodiffusion of any impurities into the furnace through the exhaust.

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Helium gas was fed, at a rate of 48 cc/minute, into the front end of the furnace tube, and the exhaust gases from the furnace were passed through a 1 N caustic trap before they were exhausted to the atmosphere, thus removing the toxic chemicals in the gas stream. The temperature of the furnace was increased from 80° to 500° C over 6 hours, at which point helium gas was bubbled through a carbon tetrachloride glass gas washing bottle (500 cc capacity) having a glass frit at the bottom of the inlet tube. The bottle was filled with CCl₄ to approximately 2/3 capacity. This treatment was continued for 60 hours.

At the end of this treatment, CCl₄ was removed from the loop and only helium gas was fed to the furnace tube at a flow rate of 250 cc/minute. The furnace was purged for 2 hours at this temperature. Then the temperature was increased to 800° C over 7 hours. At the end of this period, oxygen flow was started at a rate of 250 cc/minute, and the temperature was increased to 900° C over 5 hours, at which point this temperature was maintained for 1 hour. The temperature was then increased to 1000° C over 5 hours, followed by maintaining this constant temperature for 24 hours.

At the end of this treatment, the oxygen flow was stopped. The temperature was increased to 1150° C over 2.5 hours, followed by maintaining this constant temperature for 1 hour. The furnace temperature was then cooled down to 900° C over 11 hours, then to 80° over 10 hours. When the furnace temperature reached 80° C, the furnace was opened and the resulting fully dense silica monolith having the expected surface features was removed from the furnace. The size of the lens widths was 150 microns.

EXAMPLE 2

The steps set forth in Example 1 were repeated except that the mold was turned upside down 72 hours after casting in

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order to release the surface from the active surface.

EXAMPLE 3

The steps set forth in Example 2 were repeated except that the active surface was a gold-coated photoresist polymer having a negative sinusoidal-grating surface with a groove spacing of 5 microns. The resulting positive cast had a groove spacing of 0.8 microns.

EXAMPLE 4

The steps set forth in Example 2 were repeated except that the active surface was an assembly having a negative surface of low and high field factor microlens arrays. The mold was made of polystyrene and had surface features 600 microns in dimension. The surface features of the positive cast were 240 microns.

EXAMPLE 5

The steps set forth in Example 2 were repeated except that the active surface was a gold-coated polyester negative replica of a binary optic having several different domain types. Each domain had surface features 200 microns in dimension. The features of the positive cast were 85 microns.

Using the foregoing techniques, it is possible to create any number of articles having features of dimension 500 microns or less. Such articles include, but are not limited to reticles, mold castings, microchannel devices, micromachines, nanomachines and electronic substrates.

It will therefore be seen that we have produced novel glass and ceramic articles having feature sizes heretofore unobtainable with conventional materials. The terms and expressions employed herein are used as terms of description

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and not of limitation, and there is no intention, in the use of such terms and expressions, of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed.

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CLAIMS

1. A glass article having surface features of dimension equal to or less than 500 microns, the article produced by steps comprising:

- a. hydrolyzing and polycondensing one or more oxide precursors to form a sol comprising a plurality of oxide particles to form a sol suspended in a liquid;
- b. casting said sol into a mold having recesses of dimension equal to or less than 500 microns;
- c. gelling said sol by cross-linking said oxide particles to form a gel;
- d. aging said gel to form an aged gel;
- e. subjecting said aged gel to a drying treatment; and
- f. densifying said dried, aged gel to form a glass sol-gel monolith having smooth, curved-profile surface features and/or prismatic surface features of 500 microns or less in at least one dimension.

2. A ceramic article having surface features of dimension equal to or less than 500 microns, the article produced by steps comprising:

- a. hydrolyzing and polycondensing one or more oxide precursors to form a sol comprising a plurality of oxide particles to form a sol suspended in a liquid;
- b. casting said sol into a mold having recesses of dimension equal to or less than 500 microns;
- c. gelling said sol by cross-linking said oxide particles to form a gel;
- d. aging said gel to form an aged gel;
- e. subjecting said aged gel to a drying treatment; and
- f. densifying said dried, aged gel to form a ceramic sol-gel monolith having smooth, curved-profile surface features and/or prismatic surface features of 500 microns or less in at least one dimension.

3. The article of claim 1 wherein the steps by which the article is produced further comprise the step of metallizing the monolith with a reflective metal coating.
4. The article of claim 2 wherein the steps by which the article is produced further comprise the step of metallizing the monolith with a reflective metal coating.
5. The article of claim 3 wherein the metal is selected from the group consisting of aluminum and gold.
6. The article of claim 4 wherein the metal is selected from the group consisting of aluminum and gold.
7. The article of claim 1 wherein the article is a lens.
8. The article of claim 1 wherein the article is a lenslet.
9. The article of claim 1 wherein the article is a lens array.
10. The article of claim 1 wherein the article is a grating.
11. The article of claim 2 wherein the article is a lens.
12. The article of claim 2 wherein the article is a lenslet.
13. The article of claim 2 wherein the article is a lens array.
14. The article of claim 2 wherein the article is a grating.
15. The article of claim 1 wherein the surface features are 100 microns or less in at least one dimension.
16. The article of claim 2 wherein the surface features are 100 microns or less in at least one dimension.

17. The article of claim 1 wherein the surface features are 10 microns or less in at least one dimension.

18. The article of claim 2 wherein the surface features are 10 microns or less in at least one dimension.

19. The article of claim 1 wherein the surface features are 1 micron or less in at least one dimension.

20. The article of claim 2 wherein the surface features are 1 micron or less in at least one dimension.

21. The article of claim 1 wherein the oxide precursor is in the form of a powder.

22. The article of claim 2 wherein the oxide precursor is in the form of a powder.

23. The article of claim 1 wherein the mold has an active surface and the gel is removed from contact with the active surface before drying.

24. The article of claim 2 wherein the mold has an active surface and the gel is removed from contact with the active surface before drying.

25. The article of claim 1 wherein the glass is a multi-component glass.

26. The article of claim 1 wherein the glass is a pure silica glass.

27. A method of producing an article having surface features of dimension equal to or less than 500 microns, the article produced by steps comprising:

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- a. hydrolyzing and polycondensing one or more oxide precursors to form a sol comprising a plurality of oxide particles to form a sol suspended in a liquid;
- b. casting said sol into a mold;
- c. gelling said sol by cross-linking said oxide particles to form a gel;
- d. aging said gel to form an aged gel;
- e. subjecting said aged gel to a drying treatment comprising the steps of:
 - i. heating said aged gel in a high-humidity environment; and then
 - ii. heating said aged gel in a low-humidity environment, thereby
 - iii. removing liquid from the pores of the aged gel to form a dried, aged gel;
- f. densifying said dried, aged gel to form a sol-gel monolith having smooth, curved-profile surface features and/or prismatic surface features;
- g. creating a new mold using the monolith as a template;
- h. repeating steps (a) through (f);
- i. repeating steps (g) and (h) as many times as necessary to produce a final monolith having surface features of desired dimension.

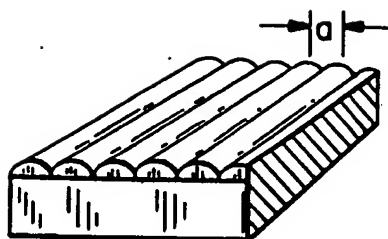


FIG. 1

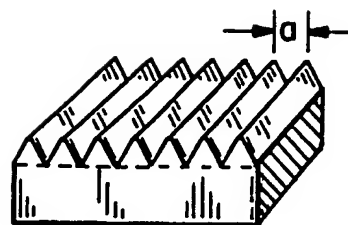


FIG. 2

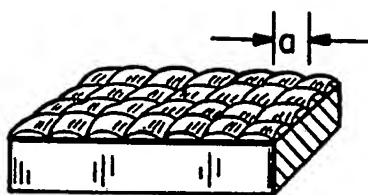


FIG. 3

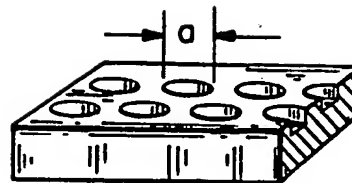


FIG. 4

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FIG. 6

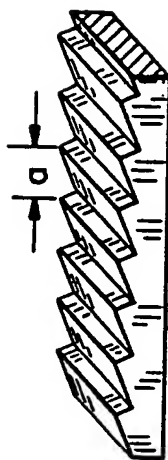


FIG. 5

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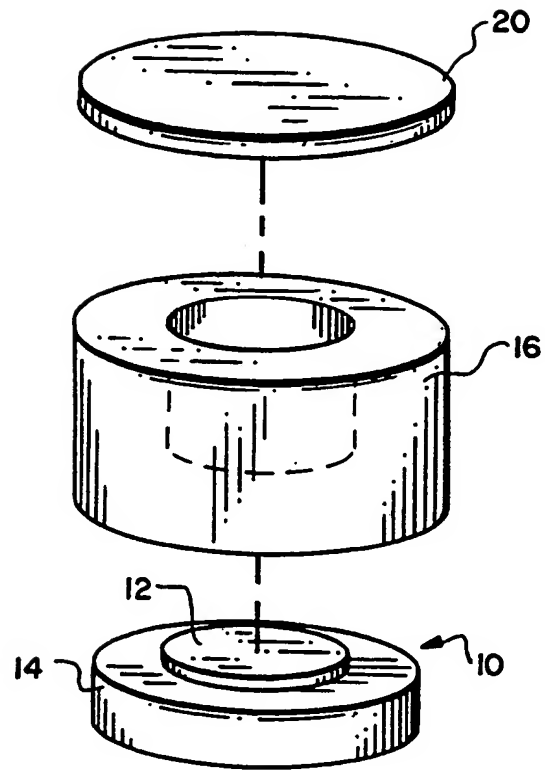


FIG. 7

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/03240

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C03C1/00; C03B19/12; C03B8/02		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C03C ; C03B ; C04B	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US,A,5 076 980 (J.L. NOGUES) 31 December 1991 cited in the application see the whole document	1,2
A	---	3-27
Y	PATENT ABSTRACTS OF JAPAN & JP,A,20 83 227 (SEIKO EPSON CORP) 23 March 1990 see abstract ---	1,2
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IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
28 JULY 1993	JUL 20 1993	
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category ^a	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
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